

# PATENT SPECIFICATION

NO DRAWINGS

1,121,595



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Date of Application and filing Complete Specification: 15 June, 1966.  
No. 26811/66.

Application made in Czechoslovakia (No. 4181) on 29 June, 1965.

Complete Specification Published: 31 July, 1968.

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Index at acceptance: —C2 C(3A13B2A1, 3A13B2E)

Int. Cl.: —C 07 c 37/22

## COMPLETE SPECIFICATION

### A Method of Purifying Phenol obtained by the Cumene Process

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## ERRATUM

SPECIFICATION No. 1,121,595

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Page 3, line 95, for "3000" read "300".

THE PATENT OFFICE  
27th January 1969

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1. produced from coal tar or brown coal tar has led to the development of new methods for producing synthetic phenol. In addition to the synthetic production processes developed earlier, in the past few years phenol has been produced by the cumene hydroperoxide method. This method consists in oxidising synthetic cumene with air or oxygen, either by a wet or by a dry process, to cumene hydroperoxide. The cumene hydroperoxide is subsequently split by the action of sulphuric acid to phenol and acetone. However, owing to side reactions there are formed, in very small quantities, a number of other substances which are partly converted to acetone and partly to phenol. These impurities have a deleterious effect on the phenol obtained, especially if the phenol is intended for further processing to polyamide fibre.

35 When the phenol is further processed to caprolactam, the impurities undergo various alterations turning finally into the so called volatile bases which are mixed with the caprolactam. Their presence in caprolactam even when in small quantities impairs the quality of the caprolactam. The admissible limit for these volatile bases expressed as the number of ml of  $n/100$  HCl consumed in titrating

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These troublesome impurities have resulted in intensive research work directed to their identification. It has been found that the main impurities of the phenol produced by the cumene process consist of: acetophenone, dimethylphenyl carbinol, 2-methylbenzofurane,  $\alpha$ -methylstyrene, mestityl oxide, diacetone alcohol, diacetyl, acetone, 2-methyl-3,4-pentanediole, methylglyoxal, and hydroxyacetone. The amount of these impurities varies within the range of 0.1—0.001% depending on the effectiveness of the columns used in fractionating the phenol from the impurities.

The presence of these impurities in phenol prepared by the cumene process can be shown by the value of the solidification point. In inferior quality phenol the value is 40.3° C, whilst high quality phenol has a solidification point of 40.9° C.

Nearly all of the methods mentioned as yet for the removal of impurities inherent in phenol prepared by the cumene process are dependent upon the fact that said impurities, especially those containing an aldehydic or keto group, such as diacetyl 4-methyl-2,3-pentanediole, methylglyoxal, hydroxyacetone and acetoin, can, under various conditions, be condensed with phenol, to form benzo-

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## COMPLETE SPECIFICATION

### A Method of Purifying Phenol obtained by the Cumene Process

We KAREL PECKA of No. 636 Senegalska, Prague 6, Czechoslovakia, JIRI MOSTECKY of No. 32 Na Petynce, Prague 6, Czechoslovakia, ZDENEK HEJDA of No. 598 Vitezneho unora, Ostrava 8, Czechoslovakia, BOHUMIR VALDAUF of No. 3 Capajevovo nam., Prague 3, Czechoslovakia all Czechoslovakian citizens. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process of purifying phenol prepared by the cumene process. The shortage of phenol, which was mostly produced from coal tar or brown coal tar has led to the development of new methods for producing synthetic phenol. In addition to the synthetic production processes developed earlier, in the past few years phenol has been produced by the cumene hydroperoxide method. This method consists in oxidising synthetic cumene with air or oxygen, either by a wet or by a dry process, to cumene hydroperoxide. The cumene hydroperoxide is subsequently split by the action of sulphuric acid to phenol and acetone. However, owing to side reactions there are formed, in very small quantities, a number of other substances which are partly converted to acetone and partly to phenol. These impurities have a deleterious effect on the phenol obtained, especially if the phenol is intended for further processing to polyamide fibre.

When the phenol is further processed to caprolactam, the impurities undergo various alterations turning finally into the so called volatile bases which are mixed with the caprolactam. Their presence in caprolactam even when in small quantities impairs the quality of the caprolactam. The admissible limit for these volatile bases expressed as the number of ml of n/100 HCl consumed in titrating

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100 g caprolactam is 5. The phenol produced by the cumene process shows however an acid consumption at least ten fold higher. Such phenol having such a high impurity content is however quite unsuitable for the production of polyamide fibre. A material containing the genetic impurities originating from the cumene process is unsuitable not only for the above said purpose, but also for a number of other processes requiring phenol for the starting product. For example in the chlorination or sulphonation of phenol, said impurities are the cause of formation of persistent coloured products and also cause trouble in the production of diene.

These troublesome impurities have resulted in intensive research work directed to their identification. It has been found that the main impurities of the phenol produced by the cumene process consist of: acetophenone, dimethylphenyl carbinol, 2-methylbenzofuran,  $\alpha$ -methylstyrene, mestityl oxide, diacetone alcohol, diacetyl, acetone, 2-methyl-3,4-pentanediole, methyl-glyoxal, and hydroxyacetone. The amount of these impurities varies within the range of 0.1—0.001% depending on the effectiveness of the columns used in fractionating the phenol from the impurities.

The presence of these impurities in phenol prepared by the cumene process can be shown by the value of the solidification point. In inferior quality phenol the value is 40.3° C, whilst high quality phenol has a solidification point of 40.9° C.

Nearly all of the methods mentioned as yet for the removal of impurities inherent in phenol prepared by the cumene process are dependent upon the fact that said impurities, especially those containing an aldehydic or keto group, such as diacetyl 4-methyl-2,3-pentanediole, methylglyoxal, hydroxyacetone and acetoin, can, under various conditions, be condensed with phenol, to form benzo-

SEE ERRATA SLIP ATTACHED

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furane, or the respective substituted homologues thereof, especially those substituted in position 2 and 3. These condensation products can be removed from crude phenol by means of steam distillation. Condensation of the ketone-type impurities, which usually are specified as benzofurane precursors with phenol, can be carried out by various methods, for example by the action of strong inorganic or organic acids, such as sulphuric acid, hydrochloric acid and phenolsulphonic acid (British Patent No. 891,561 (1962)), together with acid catalysts, such as ferric chloride and aluminium sulphate and also with bases, especially with alkali hydroxides or amines (British Patent 883,746, (1961)), or also with the aid of salts, such as chlorides, nitrates, or sulphates of various metals, such as chromium, copper and mercury. In addition to these proposals it has also been proposed to add ferric chloride (British Patent No. 920,905 (1963)).

These methods have been described in much detail, but other methods of phenol purification have been disclosed, for example the extractive distillation of crude phenol with diethyl glycol (British Patent No. 824,595 (1959)), refinement with the aid of absorbents, dehydration with dehydrating catalysts and subsequent distilling off of the olefins formed from the phenol (British Patent 802,054 (1958)). Lastly a method utilising the reaction of aldehydes and ketones with hydroxylamine, hydrazone and substituted hydrazones has been proposed.

According to the present invention there is provided a process of purifying phenol prepared by the cumene process, in which process the genetic impurities in the phenol are converted by selective hydrogenolysis of said impurities carried out in the presence of a catalyst selected from oxides and sulphides of the metals of VIth and VIIIth groups of the Periodic Table using hydrogen at a pressure of 1 to 300 atmospheres and a temperature of 180 to 450° C, the products of said selective hydrogenolysis being separated from the phenol by fractional distillation of the phenol.

The metals are preferably molybdenum, tungsten, chromium, iron, cobalt or nickel. The oxides or sulphides may be used individually or in admixture with one another. The oxides and sulphides may be supported on catalyst carriers. The hydrogenation is preferably carried out at a pressure of 3 to 50 atmospheres and at a temperature of 200 to 300° C.

The process of the invention achieves complete removal of the impurities contained in the phenol produced by the cumene process. It obviates or mitigates the difficulty found in separation of the genetic impurities of phenol in fractionating columns, since said impurities form complicated azeotropic mixtures with phenols. By selective hydrogenation accord-

ing to the present invention, the impurities are converted by way of numerous intermediates up to the corresponding hydrocarbons. These compounds do not form any azeotropic mixtures and can afterwards be easily separated from phenol by fractional distillation. However by means of the catalyst used for the selective hydrogenation of this type, the said impurities may be converted exclusively to the corresponding hydrocarbon compounds. The hydrogenation process does not alter in any way the phenol itself. The combination of hydrogenating, and dehydrogenating action which are specific to said catalysts makes possible the hydrogenolysis of the genetic impurities of phenol, especially of those having a carbonyl group in the molecule.

The process according to the invention, will now be described with reference to the following examples.

#### EXAMPLE 1

200 g crude phenol prepared by the cumene process, and containing, in addition to 0.300 wt. % mesityl oxide and 0.04 wt. % acetophenone, 16 other impurities, were added to a steel rotary autoclave of 500 ml capacity and 30 g (15 wt. %) Co-Mo-catalyst were then added to the autoclave.

The catalyst had the following composition:— CoO 3.5%; MoO<sub>3</sub> 12.5%; SiO<sub>2</sub> 0.43%; Fe<sub>2</sub>O<sub>3</sub> 0.1290%; CuO 0.06%; Al<sub>2</sub>O<sub>3</sub> 73.6%. The particle size was 2.5—4.0 mm, and the specific surface 200 m<sup>2</sup>/g. Prior to starting the experiment the catalyst was gradually heated with hydrogen to 350° C over a period of 16 hrs., hydrogen being led through at a rate of 1000 l/hour. Hydrogen was then forced into the autoclave at a pressure of up to 50 atm.

The autoclave was then heated up to 270° C, and kept at this temperature for 10 minutes. The hydrogenation product thus obtained was subjected to fractional distillation, whereupon 2.2 g (1.1 wt. %) forerun consisting predominantly of 2-methyl-pentane, cyclohexane, methylcyclopentane, cyclohexane, benzene and water, was separated out. The main distillate amounted to 192 g (96 wt. %) and contained neither mesityl oxide nor acetophenone, the total of all the impurities amounting only to 0.005 wt. %. The phenol thus obtained had a solidification point of 40.9° C.

#### EXAMPLE 2

The same apparatus and the same quantity of phenol as in Example 1 were employed. Pure molybdenumsulphide in a quantity of 30 g (15% of the phenol treated) was used. Hydrogen was then injected at a pressure of up to 50 atm, the autoclave being heated to 280° C and kept at this temperature for 10 minutes. The product obtained was subjected to fractional distillation, whereupon

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190 g (95 wt. %) of pure phenol were obtained. This phenol contained neither mesityl oxide, nor acetophenone and the content of all the impurities was below 0.005 wt. %. The phenol obtained showed a solidification point of 40.85° C.

#### EXAMPLE 3.

Again the same apparatus and initial quantity of phenol as in Example 1 were used. 20 g (10 wt. % of the phenol introduced) of pure tungsten sulphide were used as the catalyst. Hydrogen was injected at a pressure of up to 10 atm and the contents were heated to a temperature of 290° C. The hydrogenation product obtained was fractionated, and 192 g (96 wt. %) pure phenol obtained. This phenol contained no mesityl oxide. The total content of impurities only amounted to 0.0057 wt. %. The solidification point of the product was 40.80° C.

#### EXAMPLE 4.

The same apparatus as in Example 1 was employed, and the same quantity of crude phenol was processed. 20 g of a mixed catalyst containing 27% tungsten sulphide and 3% nickel sulphide supported on 70 wt. % of activated alumina was used. Hydrogen was injected in at a pressure of up to 30 atm and the mixture was heated to 250° C. The product of hydrogenation was fractionated, and 190 g (95 wt. %) pure phenol obtained. This phenol contained no mesityl oxide. The total amount of impurities was simply 0.0042 wt. %. The pure phenol showed a solidification point of 40.9° C.

#### EXAMPLE 5.

300 ml of the cobalt molybdenum catalyst as used in Example 1 was introduced to a reactor (diameter 35 mm, length 400 mm) of hydrogenation apparatus. After having reduced the catalyst the temperature was maintained at 290° C, and phenol produced by the cumene process was continuously added under pressure at a rate of 300 ml/hour. The volume load of the catalyst amounted to 1 litre per hour. The hydrogen through-flow was maintained at 100 litres per hour. The phenol introduced contained 0.182 wt. % mesityl oxide, 0.016 wt. % acetophenone, and 16 other impurities in the total amount of 0.017 wt. % (determined by chromatographic analysis). The total content of ketones in the crude phenol was 0.213 wt. % (determined colorimetrically as mesityl oxide). The hydrogenation apparatus was kept in operation continuously for 200 hours, so that altogether 60 litres of crude phenol were processed. The course of hydrogenolysis of the impurities was

continuously checked by means of colorimetric analyses of the ketone content in the hydrogenate obtained. The ketone content expressed as mesityl oxide varied within the range of 0.0032 to 0.0044 wt. % 1000 g of the product of hydrogenation thus obtained were distilled in a distillation tower with 7 theoretical plates at a reflux of 3:1. There was obtained 5.5 g overrun up to 181.4° C, and after separation of phenol 1.2 g of a neutral portion was obtained. This neutral portion contained 2-, and 3-methylpentane, methylcyclopentane, acetone, cyclohexane, benzene, cumene, methylisobutylketone, and cyclohexanol. The main fraction of 965 g consisted of pure phenol with a content of only 0.0008 wt. % of ketones (expressed as mesityl oxide). By chromatographic analysis neither mesityl oxide, nor acetophenone could be detected. The total of the other impurities amounted to only 0.014 wt. %. In the distillation flask there remained 30 g of a higher-boiling distillation residue. The phenol thus refined and distilled had a solidification point of 40.9° C it exhibited a clear white colour and was colour-stable in light. During chlorination or sulphonation no coloured products were formed.

#### WHAT WE CLAIM IS:—

1. A process of purifying phenol prepared by the cumene process, in which process the genetic impurities in the phenol are converted by selective hydrogenolysis of said impurities carried out in the presence of a catalyst selected from oxides and sulphides of the metals of VIth and VIIIth groups of the Periodic Table using hydrogen at a pressure of 1 to 3000 atmospheres and a temperature of 180 to 450° C, the products of said selective hydrogenolysis being separated from the phenol by fractional distillation of the phenol.
2. A process as claimed in Claim 1 in which the metals are molybdenum, tungsten, chromium, iron, cobalt or nickel.
3. A process as claimed in Claim 1 or 2 in which the oxides or sulphides are used individually or in admixture with one another.
4. A process as claimed in any of the preceding Claims in which the oxide and sulphides are supported on catalyst carriers.
5. A process as claimed in any of the preceding Claims in which the hydrogenation is carried out at a pressure of 3 to 50 atmospheres and a temperature of 200 to 300° C.
6. A process as claimed in any of the preceding Claims in which the impurities have a carbonyl group in the molecule.
7. A process of purifying phenol prepared by the cumene process, said process being as claimed in Claim 1 and substantially as herein

described with reference to the accompanying diagrams.

8. Phenol, when purified by the process as claimed in any one of the preceding Claims.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.  
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

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